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Photodissociation of NH_3

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Photodissociation of NH_3 through the first singlet excited state is a model problem for nonadiabatic dynamics. The electronic ground state has two C_{3v} minima connected by a D_{3h} saddle point. The excited state is quasibound in the N–H dissociation channel leading to NH_2 + H products. The ground electronic state has a conical intersection with the excited singlet electronic state, leading to competition between the adiabatic and nonadiabatic NH_2 + H pathways for dissociation:

$$NH_3(\tilde{A}\ ^1A_2'') \rightarrow \begin{cases} NH_2(\tilde{X}\ ^2B_1) + H \\ NH_2(\tilde{A}\ ^2A_1) + H \end{cases}$$

Graduate student Shikha Nangia and Professor Donald Truhlar fit analytic global diabatic potential energy surfaces using the fourfold way direct diabatization scheme. This method allows one to avoid the problem of fitting nonsmooth potentials and couplings that occur in the adiabatic representation. The direct diabatic calculations not only are efficient for fitting potential energy surfaces; they also provide a scalar, smooth, and a singularity-free representation of the potential energy surfaces and couplings for dynamical calculations.